Effects of Pyroprocessing on Performance of Geological Disposal

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Repository performance *in*sensitive to fuel-cycle application?

All other things being equal, less inventory means less risk. However, the risk reduction benefits that P-T might offer depend on the release scenario involved, and in many cases, may not be as great as a 99.9% reduction in actinide inventory might suggest.

-- L. D. Ramspott, et al., "Impacts of New Developments in Partitioning and Transmutation on the Disposal of High-Level Nuclear Waste in a Mined Geologic Repository," UCRL ID-109203, LLNL, March 1992.
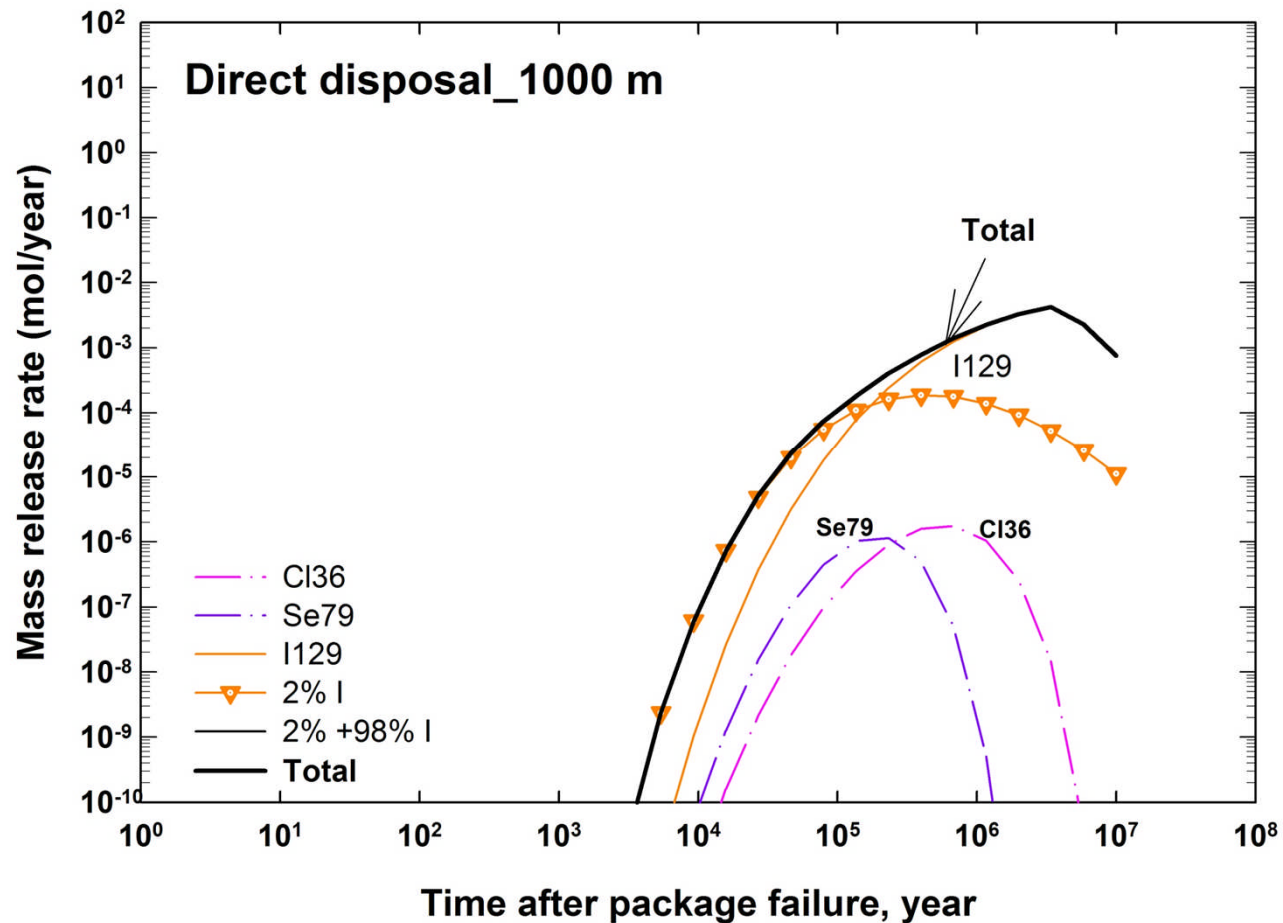
Previous studies show …(1)

- The low solubility of actinides in groundwater
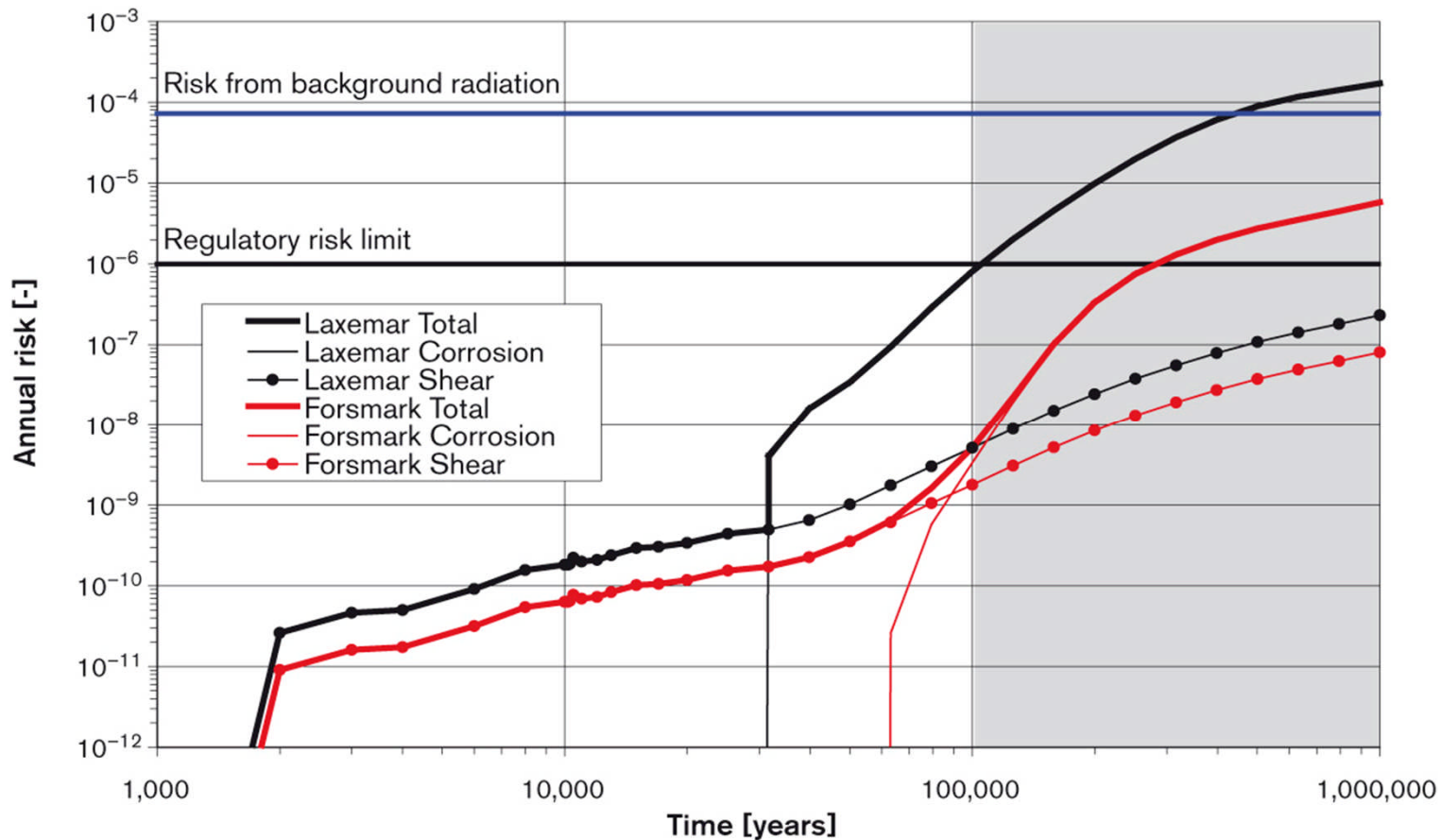

Np-237 in a vitrified HLW canister from 1 ton of LWR spent fuel
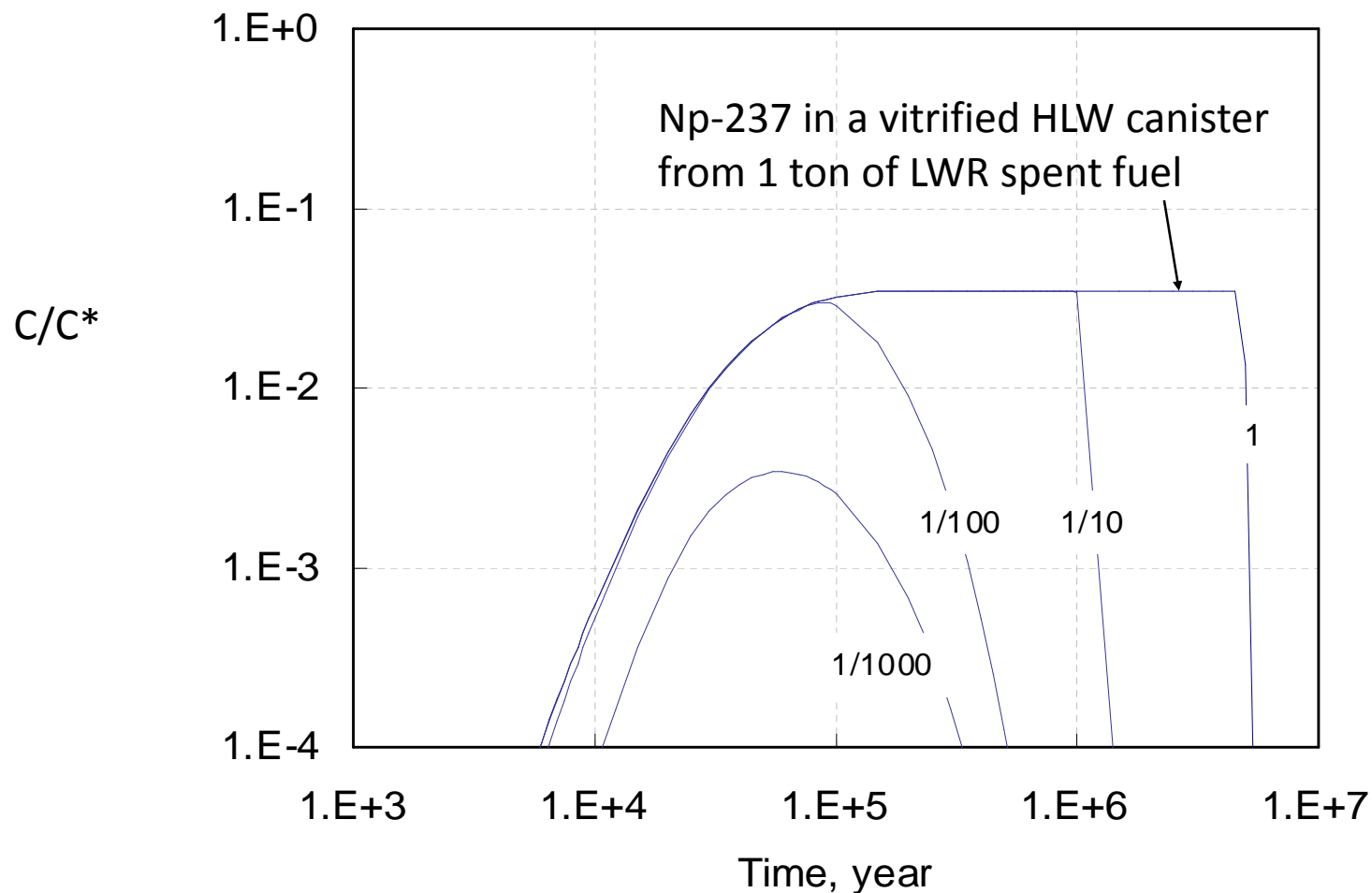
Previous studies show …(2)

- Mobile FP contributes to the dose rate.
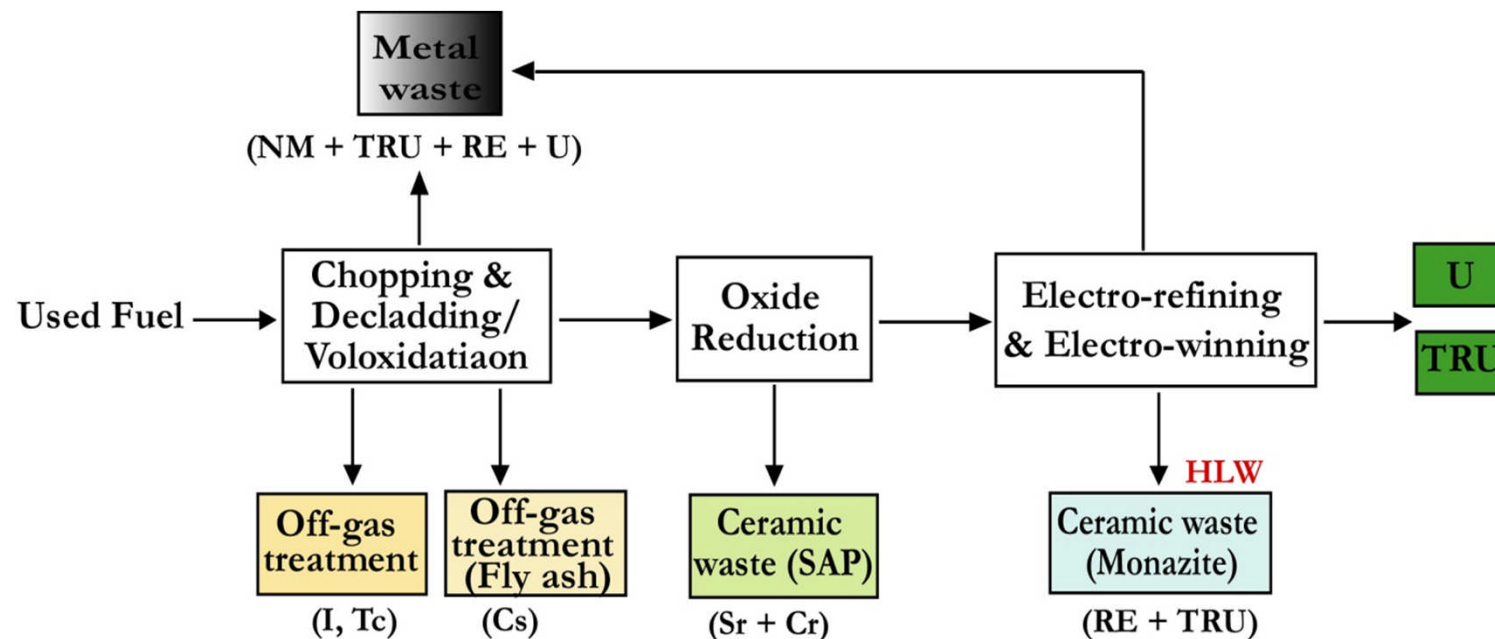
Previous studies show …

- Repository performance is already good enough.

SO, WHY PYROPROCESSING?

Pyroprocessing

(1) Pre processing & Voloxidation: Separation of mobile FP isotopes

(2) Electro-refining and winning: Separation of U, Pu and minor actinides

(3) Waste treatment and solidification

Pyroprocessing achieves

- Reduction of potential risk sources (mainly actinides)
  - by advanced separation technologies
  - (by advanced reactor/accelerator technologies)
- Better sequestration of waste materials
  - by separation of heat-emitting nuclides
  - by more durable waste forms
    - Higher waste loading
    - Lower degradation rates by groundwater
  - Smaller repository footprint
  - (by deep borehole disposal)

Emerging conceptual issues on geological disposal

- Natural Barrier or Environmental contamination
  - If radioactivity is released from the engineered barriers, it is already failure of the disposal system.
  - Success of WIPP
- Severe scenarios
  - Geological, hydro-geological, and geochemical
  - "Unknown unknowns" (Alison Macfarlane)
    - Geology is retrodictive, not predictive.

Interim storage of Spent Fuel, Pu, Minor Actinides

Opportunity of Innovation (Pyroprocessing, etc.)

Final geological disposal that realizes
- Higher robustness and safety for severe scenarios
- Minimizing reliance on "natural barriers"

FORMULATION
FOR SINGLE PACKAGE

Water contact with waste

Package failure at t_1:
   Beginning of water contact

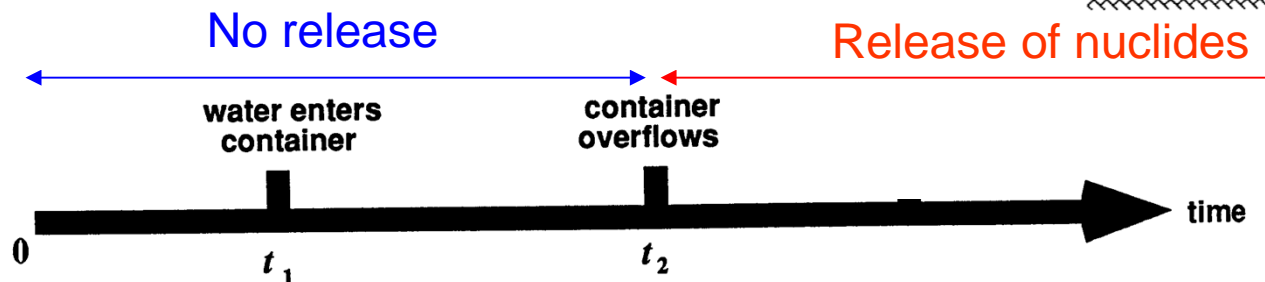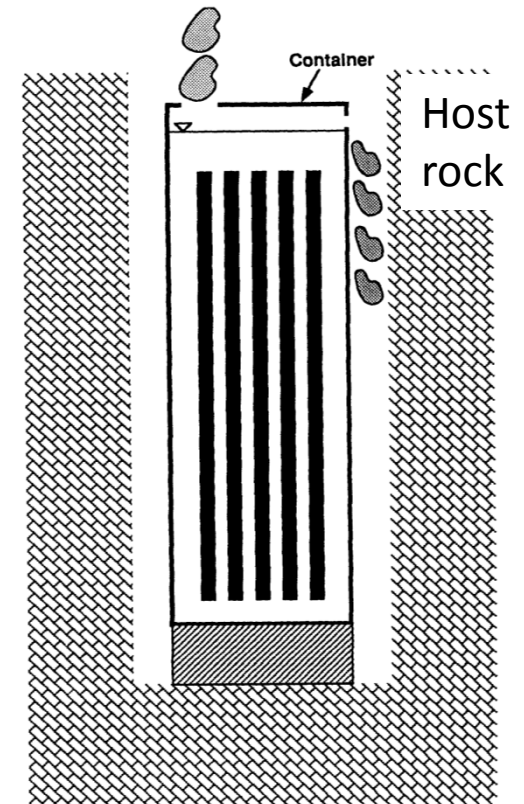Water overflow starts at t_2:
   Beginning of radionuclide release to the exterior region.
   Water is contaminated with radionuclides.

$$t_2 - t_1 = V\!/\!Q$$

V: the void volume in a package
Q: the volumetric water flow rate

Container

Host rock

No release

Release of nuclides

water enters container

container overflows

time

0   t_1 t_2

Waste matrix dissolution

Because the majority of the mass of the solidified waste is the mass of the matrix, we first consider the dissolution of the matrix. Contained radionuclides are first "released" from the matrix structure by the dissolution of the matrix.

The mass $M_w(t)$ can be written in terms of the dissolution rate, $q_w(t)$, as

$$M_w(t) = M_w^o - \int_{t_2}^{t} q_w(t') dt'$$

Assuming that $\quad q_w(t) = \dfrac{M_w^o}{T_L},\qquad$ We obtain $\quad M_w(t) = M_w^o \left(1 - \dfrac{t - t_2}{T_L} \right)$

Therefore, the fractional dissolution rate is:

$$\frac{q_w(t)}{M_w(t)} = \frac{1}{T_L - (t - t_2)}$$

Congruent release rate of radionuclide

$$\frac{dM(t)}{dt} = -\lambda M(t) - q(t), \text{ subject to } M(t_2) = M^o \exp(-\lambda t_2).$$

We assume that the fractional release rate of the nuclide is the same as that for the waste matrix, i.e., <u>congruency</u> between the matrix and the nuclide. Thus,

$$\frac{q_w(t)}{M_w(t)} = \frac{q(t)}{M(t)}$$

Therefore, $\quad q(t) = \dfrac{q_w(t)}{M_w(t)} M(t) = \dfrac{1}{T_L - (t - t_2)} M(t)$

Substituting this yields $\quad \dfrac{dM(t)}{dt} = -\left(\lambda + \dfrac{1}{T_L - (t - t_2)} \right) M(t), \text{ subject to } M(t_2) = M^o \exp(-\lambda t_2).$

The solution is $\quad M(t) = \dfrac{T_L - (t - t_2)}{T_L} M^o \exp(-\lambda t), \; t_2 \leq t \leq T_L + t_2,$

The release rate q(t) is $\quad q(t) = \dfrac{M^o}{T_L} \exp(-\lambda t), \; t_2 \leq t \leq T_L + t_2.$

Solubility-limited release of radionuclides (1)

For low-solubility isotopes, those released by the matrix dissolution cannot dissolve into the water phase completely. While the water phase is loaded at the maximum concentration, i.e., the solubility, the excess amount of released isotope will form a precipitate phase.

For the radionuclide in the precipitate phase,

For the mass, $P(t)$, of the precipitate, the balance equation is written as

$$\frac{dP}{dt} = -\lambda P - k + q(t), \ t_2 < t < T_L + t_2, \ \text{subject to } P(t_2) = 0,$$

where $\quad k \equiv QC_e^* + \lambda V C_e^* \qquad$ C*: Solubility, T_L: the waste-matrix dissolution time

Substituting this and the expression for $q(t)$, yields

$$\frac{dP}{dt} = -\lambda P - k + \frac{M^o}{T_L} \exp\left(-\lambda t\right), \ t_2 < t < T_L + t_2, \ \text{subject to } P(t_2) = 0.$$

Precipitate occurs if $\quad \left.\dfrac{dP}{dt}\right|_{t_2} > 0 \qquad$ From the above equation,

$$\left.\frac{dP}{dt}\right|_{t_2} = -\lambda P - k + \frac{M^o}{T_L}\exp\left(-\lambda t\right) = -k + \frac{M^o}{T_L}\exp\left(-\lambda t\right) > 0$$

If this is negative, then no precipitate occurs, and the radionuclide released congruently with the waste matrix can dissolve completely in the water phase in the package.

Solubility-limited release of radionuclides (2)

For time interval, $t_2 < t < T_L + t_2$, $\dfrac{dP}{dt} = -\lambda P - k + \dfrac{M^o}{T_L}\exp(-\lambda t)$, subject to $P(t_2) = 0$.
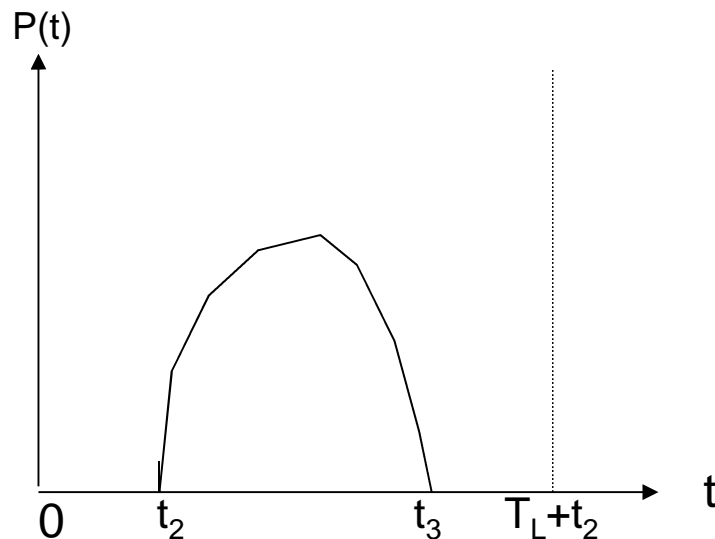
The solution is $P(t) = \dfrac{M^o}{T_L}(t - t_2)\exp(-\lambda t) - \dfrac{k}{\lambda}\left[1 - \exp(-\lambda(t - t_2))\right]$, $t_2 \le t \le T_L + t_2$

Case (1)

P(t) becomes zero at t = t_3 before T_L + t_2
(complete dissolution of the matrix)

t_3 is obtained by solving

$$\frac{M^o}{T_L}(t_3 - t_2)\exp(-\lambda t_3) - \frac{k}{\lambda}\left[1 - \exp(-\lambda(t_3 - t_2))\right] = 0$$
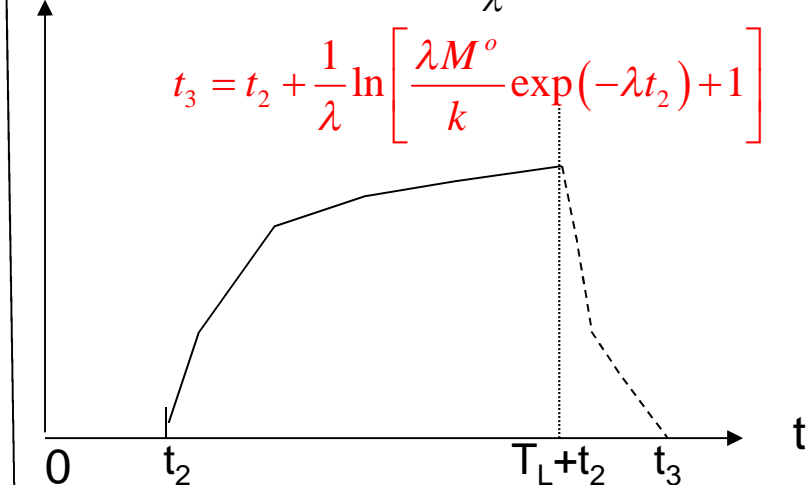
P(t)

Case (2)

P(t) becomes zero at t = t_3 after T_L + t_2.
After this time,

$$\frac{dP}{dt} = -\lambda P - k, \text{ subject to } P(t_2 + T_L).$$

From the solution,

P(t) $P(t_3) = M^o \exp(-\lambda t_3) - \dfrac{k}{\lambda}\left[1 - \exp(-\lambda(t_3 - t_2))\right] = 0$

$$t_3 = t_2 + \frac{1}{\lambda}\ln\left[\frac{\lambda M^o}{k}\exp(-\lambda t_2) + 1\right]$$

Release of Solubility-Limited Radionuclide from failed canister

$$\frac{dP}{dt}\bigg|_{t_2} = -k + \frac{M^o}{T_L}\exp(-\lambda t) > 0$$

The rate, m(t), of release of the radionuclide from the failed package is written as

$$m(t) = \begin{cases} 0, & 0 \le t \le t_2, \\ C_e^* Q, & t_2 \le t \le t_3, \end{cases}$$
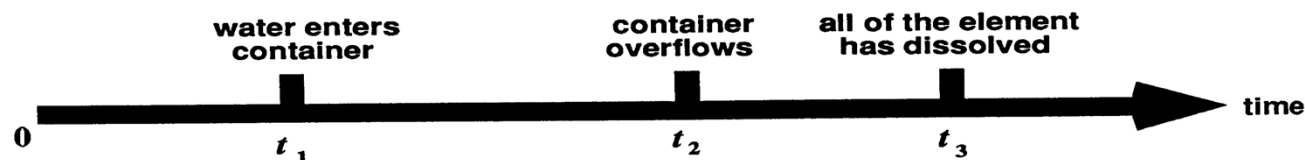
After complete dissolution of the precipitate , in-coming fresh water dilutes the water phase in the package. The governing equation for the rate of change of the isotope concentration *N(t)* in the water is

$$V\frac{dN(t)}{dt} = -\lambda V N(t) - Q N(t), \ t_3 \le t.$$

Subject to $N(t_3) = C_e^*$

The solution is given by

$$N(t) = C_e^* \exp\left\{-\left(\lambda + \frac{Q}{V}\right)(t - t_3)\right\}, \ t \ge t_3.$$

We multiply the result by *Q* to obtain the species release rate:

$$m(t) = Q C_e^* \exp\left\{-\left(\lambda + \frac{Q}{V}\right)(t - t_3)\right\}, \ t \ge t_3.$$

Radionuclides Released Congruently With Waste-Solid Alteration (1)

$$\left.\frac{dP}{dt}\right|_{t_2} = -k + \frac{M^o}{T_L}\exp(-\lambda t) \le 0$$

For time interval, $t_2 < t < t_2 + T_L$, the concentration of the radionuclide in the water in the package is governed by

$$V\frac{dN(t)}{dt} = -\lambda V N(t) - Q N(t) + q(t),\ t_2 < t < t_2 + T_L.$$

To determine the initial condition at $t = t_2$, we assume that the total mass of the radionuclide that has been released for the time interval, $t_1 < t < t_2$, is expressed as

$$\int_{t_1}^{t_2} q(t')dt' = \frac{M^o}{T_L}\int_{t_1}^{t_2}\exp(-\lambda t')dt' = \frac{M^o}{\lambda T_L}\exp(-\lambda t_1)\left[1 - \exp(-\lambda(t_2 - t_1))\right]$$

This amount is dissolved in the water of volume, V. Thus, the concentration at $t = t_2$ is written as

$$N(t_2) = \frac{M^o}{\lambda T_L V}\exp(-\lambda t_1)\left[1 - \exp(-\lambda(t_2 - t_1))\right]$$

The solution for this problem is obtained as

$$N(t) = \frac{M^o}{\lambda V T_L}\left[\exp(-\lambda t_1) - \exp(-\lambda t_2)\right]\exp\left(-\left(\lambda + \frac{Q}{V}\right)(t - t_2)\right) + \frac{M^o}{Q T_L}\exp(-\lambda t)\left[1 - \exp\left(-\frac{Q}{V}(t - t_2)\right)\right]$$

$$t_2 \le t \le t_2 + T_L$$

Radionuclides Released Congruently With Waste-Solid Alteration (2)

With this, the concentration at the time of complete dissolution of the matrix is written as

$$N\left(t_2 + T_L\right) = \frac{M^o}{\lambda V T_L}\left[\exp\left(-\lambda t_1\right) - \exp\left(-\lambda t_2\right)\right]\exp\left(-\left(\lambda + \frac{Q}{V}\right)T_L\right) + \frac{M^o}{Q T_L}\exp\left(-\lambda\left(t_2 + T_L\right)\right)\left[1 - \exp\left(-\frac{Q}{V}T_L\right)\right]$$

After the matrix has dissolved, and the radionuclide is all in the water in the package, the governing equation is written as

$$V\frac{dN(t)}{dt} = -\lambda V N(t) - Q N(t),\ t > t_2 + T_L.$$

The solution is written as

$$N(t) = N\left(t_2 + T_L\right)\exp\left(-\left(\lambda + \frac{Q}{V}\right)\left(t - t_2 - T_L\right)\right)$$

$$= \frac{M^o}{\lambda V T_L}\left[\exp\left(-\lambda t_1\right) - \exp\left(-\lambda t_2\right)\right]\exp\left(-\left(\lambda + \frac{Q}{V}\right)\left(t - t_2\right)\right)$$

$$+ \frac{M^o}{Q T_L}\left[1 - \exp\left(-\frac{Q}{V}T_L\right)\right]\exp\left(-\lambda t\right)\exp\left(-\frac{Q}{V}\left(t - t_2 - T_L\right)\right),\ t \geq t_2 + T_L$$

Radionuclides Released Congruently With Waste-Solid Alteration (3)

With these results, the rate of release from the package is written as

$$m(t) = 0, \ 0 \le t \le t_2,$$

$$m(t) = \frac{M^o Q}{\lambda V T_L} \left[\exp(-\lambda t_1) - \exp(-\lambda t_2) \right] \exp\left(-\left(\lambda + \frac{Q}{V} \right)(t - t_2) \right)$$

$$+ \frac{M^o}{T_L} \exp(-\lambda t) \left[1 - \exp\left(-\frac{Q}{V}(t - t_2) \right) \right] \qquad t_2 \le t \le t_2 + T_L$$

$$m(t)$$

$$= \frac{M^o Q}{\lambda V T_L} \left[\exp(-\lambda t_1) - \exp(-\lambda t_2) \right] \exp\left(-\left(\lambda + \frac{Q}{V} \right)(t - t_2) \right)$$

$$+ \frac{M^o}{T_L} \left[1 - \exp\left(-\frac{Q}{V} T_L \right) \right] \exp(-\lambda t) \exp\left(-\frac{Q}{V}(t - t_2 - T_L) \right), \ t \ge t_2 + T_L$$

	Normal Scenario		Severe scenario	
	Direct disposal	Pyro-processing	Direct disposal	Pyro-processing
Eh(mV)	-194		600	
Solubility of Np (mol/m^3)	3.5E-06		7.0E-03	
Porosity of the host rock, ε	0.02		0.2	
Pore velocity of groundwater, v (m/yr)	1		10	
Cross-sectional area of waste package for water flow, a (m^2)	0.03		3	
Volumetric water flow rate through a package, $Q = \varepsilon v a$ (m^3/yr)	6E-4		6	
Water volume in the package at t$_1$, V (m^3)	3			
$t_2 - t_1 = \dfrac{V}{Q}$ (yr)	5E3		0.5	
Package failure time, t_1 (yr)	75,000		1,000	
Waste-form alteration time*, T_L (yr)	1E9	1E8	1E6	
Number of packages for 20,000 MTHM	10,000	500	10,000	500
Inventory of Np in a package at t_2 (mol)	20	0.4	20	0.4
$\dfrac{M^o}{T_L}\exp(-\lambda t)$ (mol/yr)	2E-8	4E-9	2E-5	4E-7
$k \equiv QC_e^* + \lambda V C_e^*$ (mol/yr)	2.1E-9		4.2E-2	
Release mode	Solubility limited		Congruent	
Complete precipitate dissolution time, t_3 (yr)	2.5E7	1.3E7	-------	

FORMULATION
FOR ENTIRE REPOSITORY

Repository configurations

- 20,000 MTHM spent fuel.
- Footprint per package:
  - 100 m^2 for spent fuel
  - 20 m^2 for pyro HLW
- Total repository footprint:
  - 100 m^2 x 10,000 = 1,000,000 m^2 = 1000^2 m^2 for spent fuel
  - 20 m^2 x 500 = 10,000 m^2 = 100^2 m^2 for pyro HLW (factor of 100 smaller)

Model concept

$\varphi(t)$ [kg/m^{2}yr]   Radionuclide from the repository
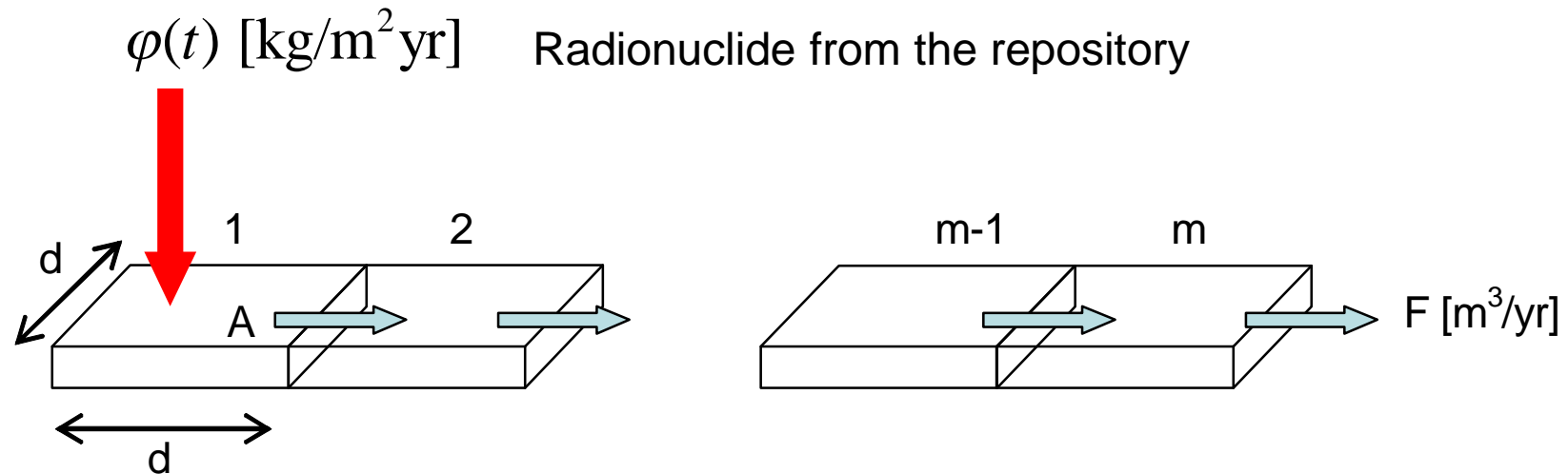
The geological medium is divided into *m* compartments. Each compartment has the same volume, *V* [m³], and consists of rock pores and rock matrix. A compartment has dimensions of *d* [m] x *d* [m] x *h* [m]. Compartments are connected by groundwater flow through rock pores. The groundwater flow rate, *F* [m³/yr], is assumed to be the same throughout the *m* compartments.

Sorption equilibrium in compartment 1

In Compartment 1, the rock pores and the rock matrix occupy the volumes of $\varepsilon_1 V$ and $(1- \varepsilon_1) V$, respectively, where ε_1 is the porosity of the rock of the first compartment. By the assumption of the saturated medium, the rock pores are filled with water. We define two concentrations of the radionuclide in the compartment:

$N_1 (t)$:   concentration of radionuclide in the water phase in the pores in compartment 1 [mol/m³]

$S_1 (t)$:   concentration of radionuclide in the rock-solid phase in compartment 1 [mol/kg]

Between two concentrations, we assume sorption equilibrium:

$$S_1 = Kd_1 N_1 \qquad (1)$$

Kd_1 is the sorption distribution coefficient for the radionuclide.

The mass $M_1(t)$ [kg] of the radionuclide existing in compartment 1 either in the water phase or in the solid phase of the rock is written as

$$M_1(t) = V \varepsilon_1 N_1 (t) + V \left(1 - \varepsilon_1 \right) \rho_1 S_1(t) \qquad (2)$$

ρ_1 is the density of the medium [kg/m³].

Retardation factor for nuclide

From (2), $\quad M_1(t) = \left[V\varepsilon_1 + V(1-\varepsilon_1)\rho_1 Kd_1\right]N_1(t) = V\varepsilon_1\left[1 + \dfrac{(1-\varepsilon_1)}{\varepsilon_1}\rho_1 Kd_1\right]N_1(t) \quad$ (3)

The [ ] part is known as the retardation factor, R_1. Thus,

$$M_1(t) = V\varepsilon_1 R_1 N_1(t) \tag{4}$$

where $\quad R_1 \equiv 1 + \dfrac{(1-\varepsilon_1)}{\varepsilon_1}\rho_1 Kd_1 \qquad$ Retardation factor $\qquad$ (5)

Mass balance in compartment 1

$$\frac{dM_1}{dt} = \varphi(t)A - FN_1(t) - \lambda M_1 \qquad (6)$$

Substituting (4) into (6) yields

$$\frac{dN_1(t)}{dt} = \frac{\varphi(t)A}{V\varepsilon_1 R_1} - \left\{ \frac{F}{V\varepsilon_1 R_1} + \lambda \right\} N_1(t) \qquad (7)$$

Define the following parameters: $\qquad \mu_1 \equiv \frac{F}{V\varepsilon_1 R_1}; \ \xi \equiv \frac{A}{F} \qquad (8)$

$$\frac{dN_1(t)}{dt} = \mu_1 \xi \varphi(t) - \left\{ \mu_1 + \lambda \right\} N_1(t), \ t > 0, \ N_1(0) = 0, \qquad (9)$$

Balance equations

$$\frac{dN_1(t)}{dt} = \mu_1 \xi \varphi(t) - \left\{ \mu_1 + \lambda \right\} N_1(t), \ t > 0, \ N_1(0) = 0,$$

$$\frac{dN_2(t)}{dt} = \mu_2 N_1(t) - \left\{ \mu_2 + \lambda \right\} N_2(t), \ t > 0, \ N_2(0) = 0,$$

$$\frac{dN_m(t)}{dt} = \mu_m N_{m-1}(t) - \left\{ \mu_m + \lambda \right\} N_m(t), \ t > 0, \ N_m(0) = 0,$$

For the release function, we consider the following two cases:
(i) Congruent release case

$$\varphi(t) = \varphi_o \exp\left(-\lambda t\right)\left[h(t - t_2) - h(t - t_2 - T_L) \right]$$

(ii) Solubility-limited release case

$$\varphi(t) = \bar{\varphi}\left[h(t - t_2) - h(t - t_3) \right]$$

Release rates from *m*-th compartment

$$f\left(t\right) \ [\text{mol/yr}] = FN_m(t)$$

(for congruent release)

$$f(t) = N \frac{M_o}{T_L} \exp\left(-\lambda t\right)\left[h(t-t_2)P\left(m,\mu\left(t-t_2\right)\right) - h(t-t_2-T_L)P\left(m,\mu\left(t-t_2-T_L\right)\right)\right]$$

(for solubility-limited release)

$$f(t) = NC^*Q\left[h(t-t_2)P\left(m,\left(\mu+\lambda\right)\left(t-t_2\right)\right) - h(t-t_3)P\left(m,\left(\mu+\lambda\right)\left(t-t_3\right)\right)\right]$$

Here, the incomplete Gamma function with *m* as an integer is defined as

$$P(m,x) \equiv \frac{1}{\Gamma(m)}\int_0^x \tau^{m-1}\exp\left(-\tau\right)d\tau = 1 - \sum_{k=1}^m \exp(-x)\frac{x^{k-1}}{(k-1)!}$$
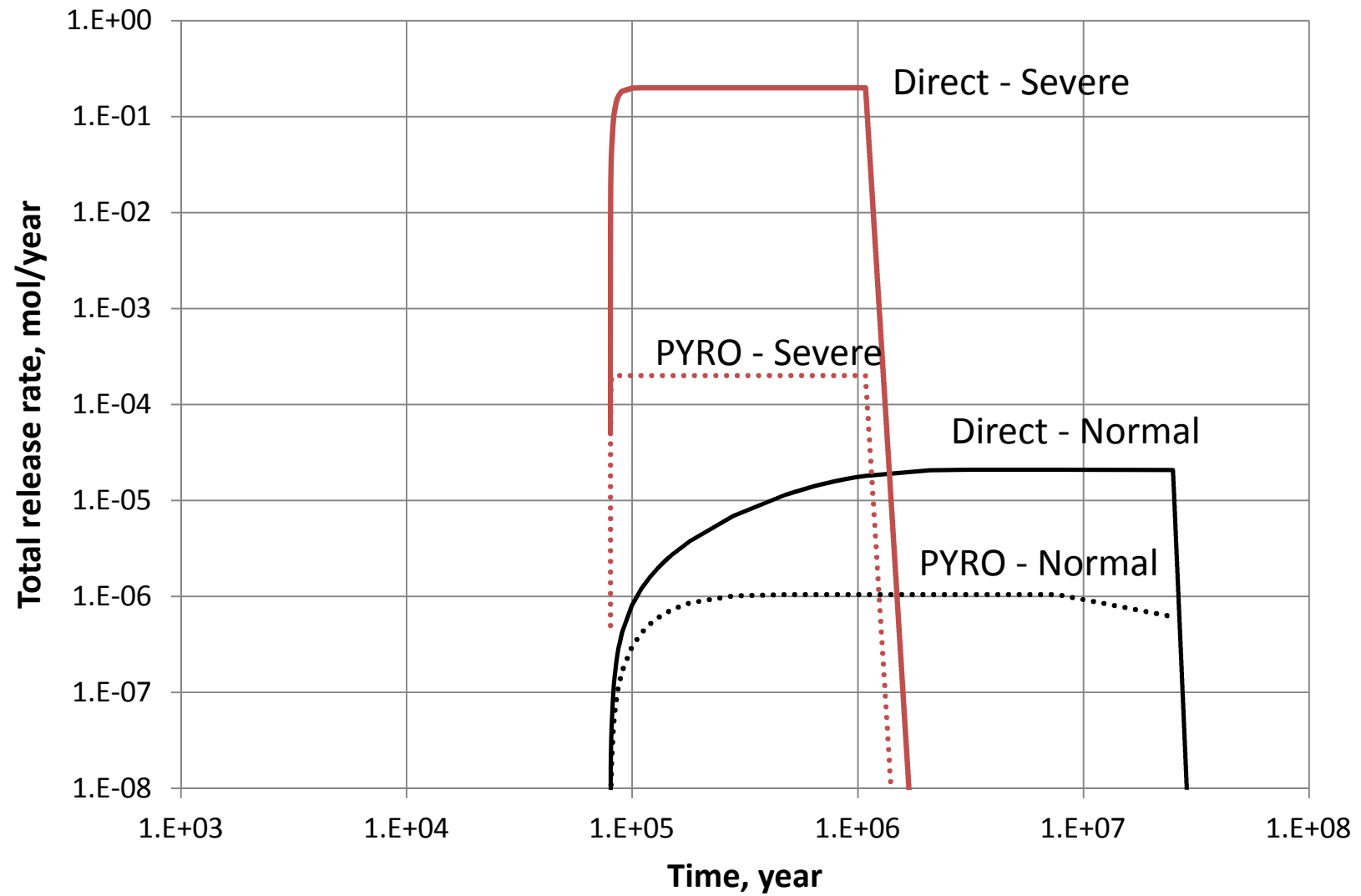
Observations

- In the solubility-limited regime, reduction of total number of packages directly decreases the total release rate to the environment.

- In the congruent release regime, both total number of packages AND initial mass loading in each package directly result in the environmental impact.

Closing remarks

– Smaller repository has clear advantage in the environmental burden in the normal scenarios.

– Robust waste form and smaller initial mass loading are effective to mitigate the severe scenarios.

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